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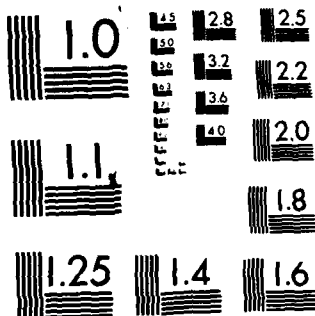
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which is a substrate-induced effect. The lineshape variation of the S photoemission features along a particular band is a dramatic function of SBZ position, and is directly related to the presence of projected Fe sp-levels at the same  $k_{\parallel}$ . These line width variations match the predictions of Liebsch for c(2x2)O/Ni(100), and indicate that the s(3p<sub>z</sub>)-Fe(sp) interaction is a principal component of the S-Fe bond on Fe(100). Thus, the correlation of the  $k_{\parallel}$ -dependence of adsorbate level dispersions and linewidths provides new information about the bonding character of chemisorption systems.

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The Electronic Structure of  $c(2 \times 2)S/Fe(100)$ :  
S 3p-Level Dispersions and Linewidths

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### Abstract

↙ The electronic structure of segregated  $c(2 \times 2)S/Fe(100)$  <sup>was</sup> ~~has~~ been determined using synchrotron radiation and angle-resolved photoemission. In addition to mapping the S 3p-derived energy bands, the lineshapes of the S photoemission features were correlated to their surface Brillouin zone (SBZ) <sup>position.</sup> The <sub>3 Pauli X Pauli y</sub> dispersions of the bands derived from in-plane S 3p<sub>x</sub>p<sub>y</sub> levels are induced by S-S interactions, and are well described by a tight-binding model. The S 3p<sub>z</sub>-derived band is anomalously wide (1.2 eV) compared to the tight-binding width, which is a substrate-induced effect. ↙ The lineshape variation of the S photoemission features along a particular band is a dramatic function of SBZ position, and is directly related to the presence of projected Fe sp-levels at the same  $\vec{k}_{\parallel}$ . These line width variations match the predictions of Liebsch for  $c(2 \times 2)O/Ni(100)$ , and indicate that the S(3p<sub>z</sub>)-Fe(sp) interaction is a principal component of the S-Fe bond on Fe(100). Thus, the correlation of the  $\vec{k}_{\parallel}$ -dependence of adsorbate level dispersions and linewidths provides new information about the bonding character of chemisorption systems.

## I. INTRODUCTION

The presence of S in Fe and its alloys is of fundamental engineering importance. The poisoning of catalytic Fe surfaces,<sup>1</sup> and the embrittling of alloy steels by grain boundary segregation<sup>2</sup> are the most striking examples of sulfur's detrimental effect in industrial practice. To physically describe these processes, it is necessary to know the details of the S-Fe interaction. The advent of angle-resolved ultraviolet photoemission spectroscopy (ARUPS) as a tool for the measurement of the electronic structure of adsorbates has provided a real step towards answering such questions.<sup>3</sup> Coupled with an appropriate theoretical model, the microscopic details of adsorbate-substrate bonding may be inferred from these measurements. For the S-Fe system, it is natural to first study layers of S on Fe single crystal surfaces. In particular,  $c(2 \times 2)\text{S}/\text{Fe}(100)$  is a well-characterized, easily prepared surface.<sup>4</sup> In addition, extensive ARUPS studies of  $\text{S}/\text{Ni}(100)$  have been performed,<sup>5</sup> allowing for an immediate comparison with  $\text{S}/\text{Fe}(100)$ .

It has been pointed out by Liebsch<sup>6</sup> that adsorbate-substrate bonding may be identified by both the electronic band structure of the adsorbate levels, and the lineshape variation along these bands. This report describes an ARUPS study of the electronic structure and linewidth features of the 3p levels of S in the  $c(2 \times 2)/\text{Fe}(100)$  configuration. The hybridization of the S 3p bands, and the variation of the S 3p photoemission lineshapes with their position in the surface Brillouin zone (SBZ) indicate that S bonds on  $\text{Fe}(100)$  principally through the S ( $3p_z$ )-Fe(sp)

interaction. This is in direct contrast to S/Ni(100), where bonding is found to be primarily through the Ni(3d) electrons.<sup>5</sup>

## II. EXPERIMENTS

The Tantalus I storage ring of the University of Wisconsin Synchrotron Radiation Center was used as the photon source. The University of Pennsylvania toroidal grating monochromator<sup>7</sup> was used for wavelength selection, while an angle-resolved analyzer<sup>8</sup> of  $\pm 2.5^\circ$  angular acceptance was used for electron collection. The net resolution of the analyzer and beam line optics was nominally 0.4 eV, defined as the 10%-90% width of the Fe Fermi edge. Standard  $\vec{A} \cdot \vec{p}$  matrix element theory was used to symmetry-select the initial emission states.<sup>3</sup>

The c(2x2)S/Fe(100) surface was prepared by annealing a clean Fe(100) crystal containing ~20 ppm S at 900 K for approximately 15 hours. This procedure was repeated several times, with reproducible results attained.

Smooth backgrounds were subtracted from the measured photoemission spectra, and the S features were deconvoluted by Gaussian fitting. Lineshape broadening effects due to the finite angular acceptance of the analyzer used was subtracted from the measured linewidths. This broadening varied with the  $k_{\parallel}$ -derivative of the band dispersions, and was ~150 meV for the steepest dispersing band.

## III. RESULTS

The real space unit cells and SBZ's of clean Fe(100) and c(2x2)S/Fe(100) are depicted in Fig. 1. For brevity, the following discussion will be concerned with the  $\bar{\Gamma}\bar{M}$  direction only. The



results along the other high symmetry lines of the SBZ lead to the same conclusion as those presented here.<sup>9</sup> The measured S 3p-derived bands are shown in Figs. 2 and 3, denoted by their symmetry with respect to the mirror plane of detection. In addition, the levels at  $\bar{\Gamma}$  are labelled by the orbital character of the S 3p-wavefunctions at that point. The cross-hatching in the even-band figure shows the projection of the Fe sp-bands lying below  $\bar{\Gamma}\bar{M}$ .<sup>9</sup> It can be seen that there is the appropriate reflection symmetry about the zone edge  $\bar{M}$ . The degeneracy of the  $p_x$ - and  $p_y$ -derived bands at  $\bar{\Gamma}$  and  $\bar{M}$ , which is dictated by the  $C_{4v}$  symmetry of the  $c(2 \times 2)S/Fe(100)$  geometry, is also experimentally verified.

The odd band has a cosine-like dispersion which is characteristic of a tight-binding band. A tight-binding calculation for a square 2-D array of S in the  $c(2 \times 2)/Fe(100)$  geometry yields a bandwidth along  $\bar{\Gamma}\bar{M}$  of 2.2 eV.<sup>10</sup> The order of magnitude agreement of this result with the experimental value (1.4 eV), along with the band shape, imply that the bands derived from S 3p orbitals in the surface plane are dominated by S-S interactions.

The even bands show that the  $p_x$ - and  $p_z$ -derived bands have hybridized upon crossing, with the  $p_z$ -derived band now dispersing up in energy by 1.2 eV. If the tight-binding calculation mentioned previously is scaled to the measured  $p_y$ -derived band, a dispersion of .5 eV would be predicted for the  $p_z$ -derived band. The actual dispersion, then, must arise from S interactions with the Fe substrate. This is not surprising, as the  $p_z$  orbitals are grossly distorted by the presence of the Fe surface.

Similar results are seen for  $c(2 \times 2)S/Ni(100)$ <sup>5</sup>, but with some subtle differences. For one, there is a problem in  $p_x$ -band scaling. The measured odd bandwidth along  $\bar{\Gamma}\bar{M}$  for  $S/Ni(100)$  is also 1.4 eV, yet the S-S spacing is 12% smaller for  $S/Ni$  than for  $S/Fe$  (3.57 Å vs. 4.06 Å). Coupled with the fact that a  $p(2 \times 2)S$  layer will form on  $Ni(100)$ ,<sup>10</sup> but not on  $Fe(100)$ , these differences already suggest varied bonding features for the two surfaces.

The linewidths of the odd-level S photoemission features remain constant across  $\bar{\Gamma}\bar{M}$ , with a full width at half-maximum (FWHM) of  $1 \pm .15$  eV (see Fig. 2b). This result differs from  $c(2 \times 2)S/Ni(100)$ , where a linear increase in FWHM with binding energy is seen.<sup>5</sup> In both the Fe and Ni case, the odd bands are split-off from projected bulk levels, hence any broadening variation across the SBZ should be the result of the energy-dependence of an Auger-decay mechanism.<sup>5</sup> The fact that this broadening is seen on Ni, but not on Fe reflects differences in their respective densities of states. XPS measurements have shown that over the energy range of the S 3p binding energies, the gradient of the occupied Fe density of states (DOS) is considerably less than for the Ni DOS.<sup>11</sup> Also, appearance potential spectroscopy has shown that the unoccupied DOS of Fe and Ni vanish within 2 eV of the Fermi energy.<sup>12</sup> Since the lifetime of the hole created in the photoexcitation process is proportional to the convolution of the occupied and unoccupied DOS, it is plausible that there is no energy dependence of the Auger decay rate on Fe.

In contrast, Figs. 4 and 5 display the linewidths along the

"p<sub>z</sub>" and "p<sub>x</sub>" bands, respectively. (Note: The quotes appearing here have been introduced for notational convenience in the discussion to follow, and refer to the orbital character of the S levels appearing at  $\bar{\Gamma}$  in the hybridized bands of Fig. 2.) The cross-hatching indicates where the bands emerge from the projected Fe sp-bands, as determined from Fig. 2. With the ambiguities present in the peak deconvolution procedure, as well as experimental resolution, the uncertainty in the data is  $\pm 10\%$ . Therefore, the smooth lines in these figures are only an aid in following the most important trends, namely:

- o The widths of the levels along the "p<sub>z</sub>" band are large when the levels lie over projected Fe bands, and small otherwise.
- o The peak width along the "p<sub>x</sub>" band is narrowest at  $\bar{\Gamma}$ , and again at  $\bar{M}$ . Broadening takes place only when this band lies over the projected bands.
- o The narrowest peaks appear at  $\bar{M}$ , with approximately the same width as those measured along the split-off odd band. Note that, at  $\bar{M}$ , both even bands are also split-off from the projected bulk bands.

This behavior is not seen for S/Ni(100), and has not been reported for any other substrate-adsorbate system.

#### IV. DISCUSSION

The fact that the S 3p lineshape broadening is directly related to the position of the 3p-levels relative to projected Fe sp-levels indicates that there is strong adsorbate-substrate mixing through these levels. The SBZ variation of adsorbate p-level broadening has been predicted by Liebsch, who used a layer-

KKR, multiple-scattering method to calculate the electronic structure and lineshape behavior of  $c(2 \times 2)O/Ni(100)$ .<sup>6</sup> Liebsch's results for the O bands along  $\bar{\Gamma}\bar{M}$  are reproduced in Figure 6, which shows the partial-wave projections of the local density of states at an oxygen site. The salient features are:

- o The odd band( $p_y$ ) level disperses across the SBZ with a  $\delta$ -function width, since this band is split-off from any projected Ni bands of the same symmetry. This is similar to the results for the odd S band on Fe(100), where no broadening variation was seen. The residual 1 eV width must come from a combination of natural linewidth, experimental resolution, or decay mechanisms not due to the S 3p-Fe(sp) interaction.

- o The  $p_z$ -derived level is the bonding level at  $\bar{\Gamma}$ , and has been broadened considerably. As it disperses across the SBZ, hybridization occurs with the even  $p_x$  band, and is hard to resolve in this region. Once it crosses out of the projected bands, however, the width reverts to the split-off,  $\delta$ -function width of the odd bands. This same qualitative behavior was noted in Figure 3 for the S 3p<sub>z</sub>-derived band.

- o At  $\bar{\Gamma}$ , the  $p_x$ -derived level is not broadened, because the O( $p_x$ ) and Ni(sp) levels do not mix for symmetry reasons. Upon leaving  $\bar{\Gamma}$ , the  $p_x$ -derived level no longer has full  $p_x$ -symmetry, and broadens by mixing with the Ni(sp) levels. Once it has crossed out of the projected Ni bands, however, this level again returns to the split-off width. This description qualitatively agrees with the measured results of Fig. 4.

The above discussion indicates strongly that an important

component of the S-Fe bond on Fe(100) is through the S(3p)-Fe(sp) interaction and that the main S bonding orbital is the  $3p_z$ . This is in contrast to the conclusions reached in similar experiments conducted for S/Ni(100) where the S-metal bond is mediated by the S(3p)-Ni(3d) interaction.<sup>5</sup> Because of the more open nature of the bcc(100) vs. fcc(100) surface, the distance between a S atom and the metal atom lying directly below it is much smaller for S/Fe than for S/Ni (from LEED results, these distances are  $2.52 \text{ \AA}$  and  $3.05 \text{ \AA}$ , respectively.) This geometric difference may partially explain the bonding differences seen for chemisorbed S on the two surfaces. This is especially true for the participation of the S  $3p_z$  orbital in the S-metal bond.

#### ACKNOWLEDGEMENTS

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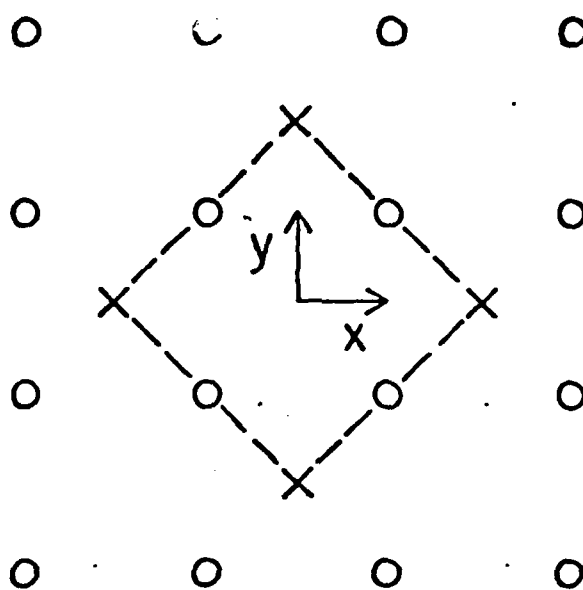
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### Figure Captions

- Fig. 1      a) Real space unit cell and b) Surface Brillouin zones of Fe(100) and c(2x2)S/Fe(100). (X's are S atoms.)
- Fig. 2      a) Odd S 3p-derived band along  $\bar{\Gamma}\bar{M}$ ; b) S level widths along this band.
- Fig. 3      Even S 3p-derived bands along  $\bar{\Gamma}\bar{M}$ .
- Fig. 4      S 3p-level widths along lower band of Fig. 3.
- Fig. 5      S 3p-level widths along upper band of Fig. 3.
- Fig. 6      The  $k_{\parallel}$ -dependence of the projected local density of states at an oxygen site for c(2x2)O/Ni(100). Reprinted from Liebsch.<sup>6</sup>

(a) SURFACE UNIT CELL



(b) SURFACE BRILLOUIN ZONES

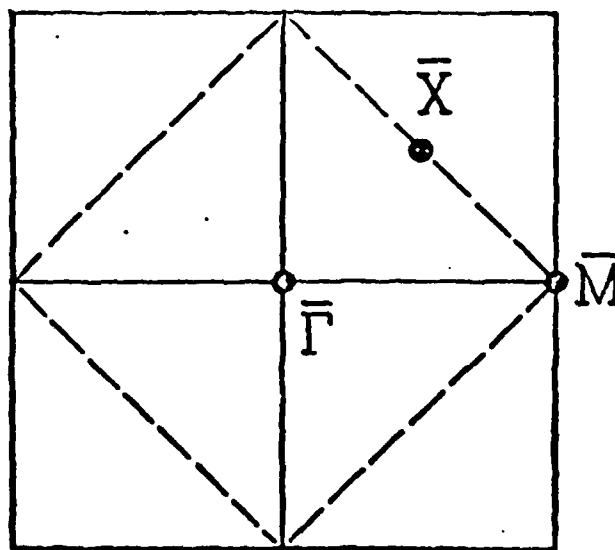


FIG. 1



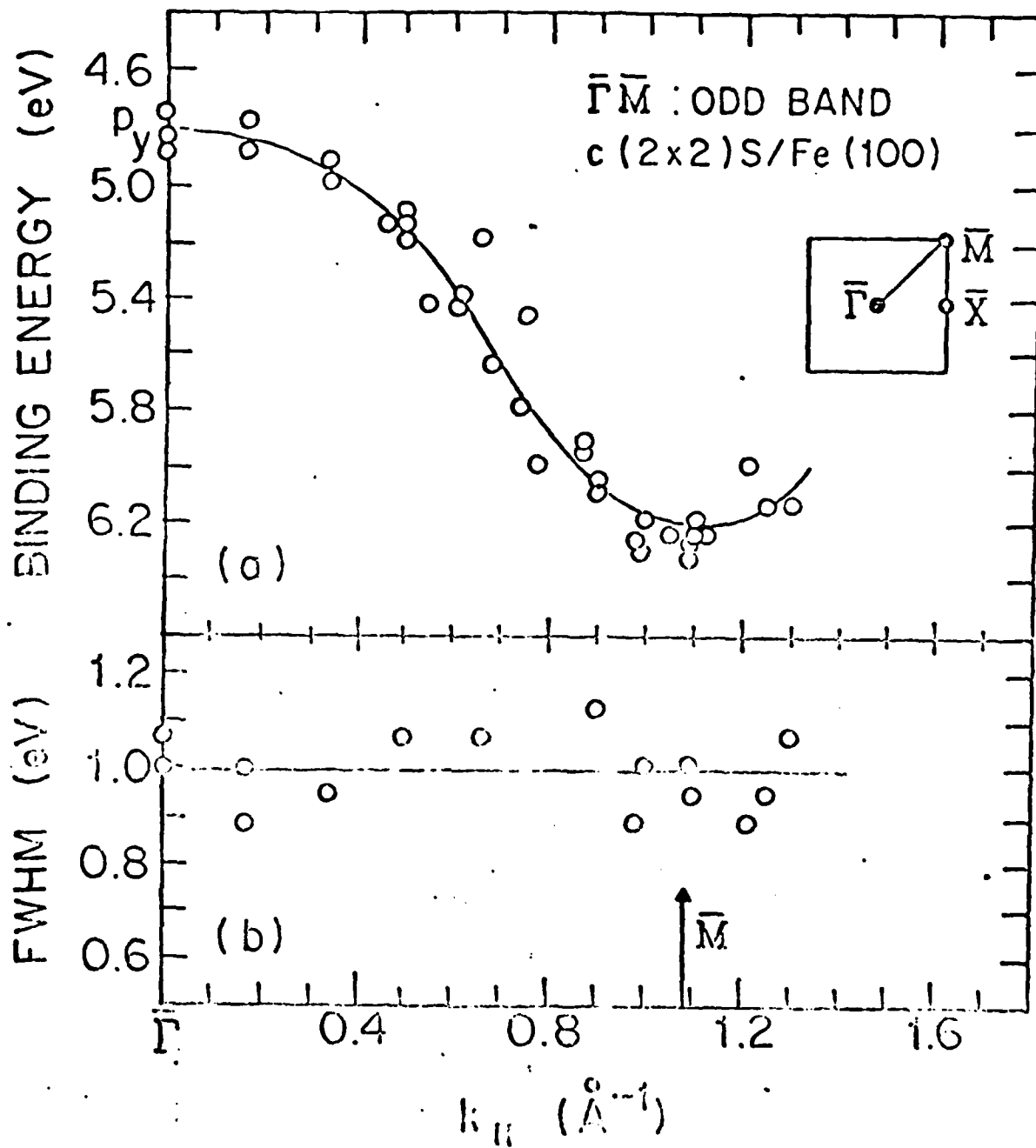


FIG. 2.

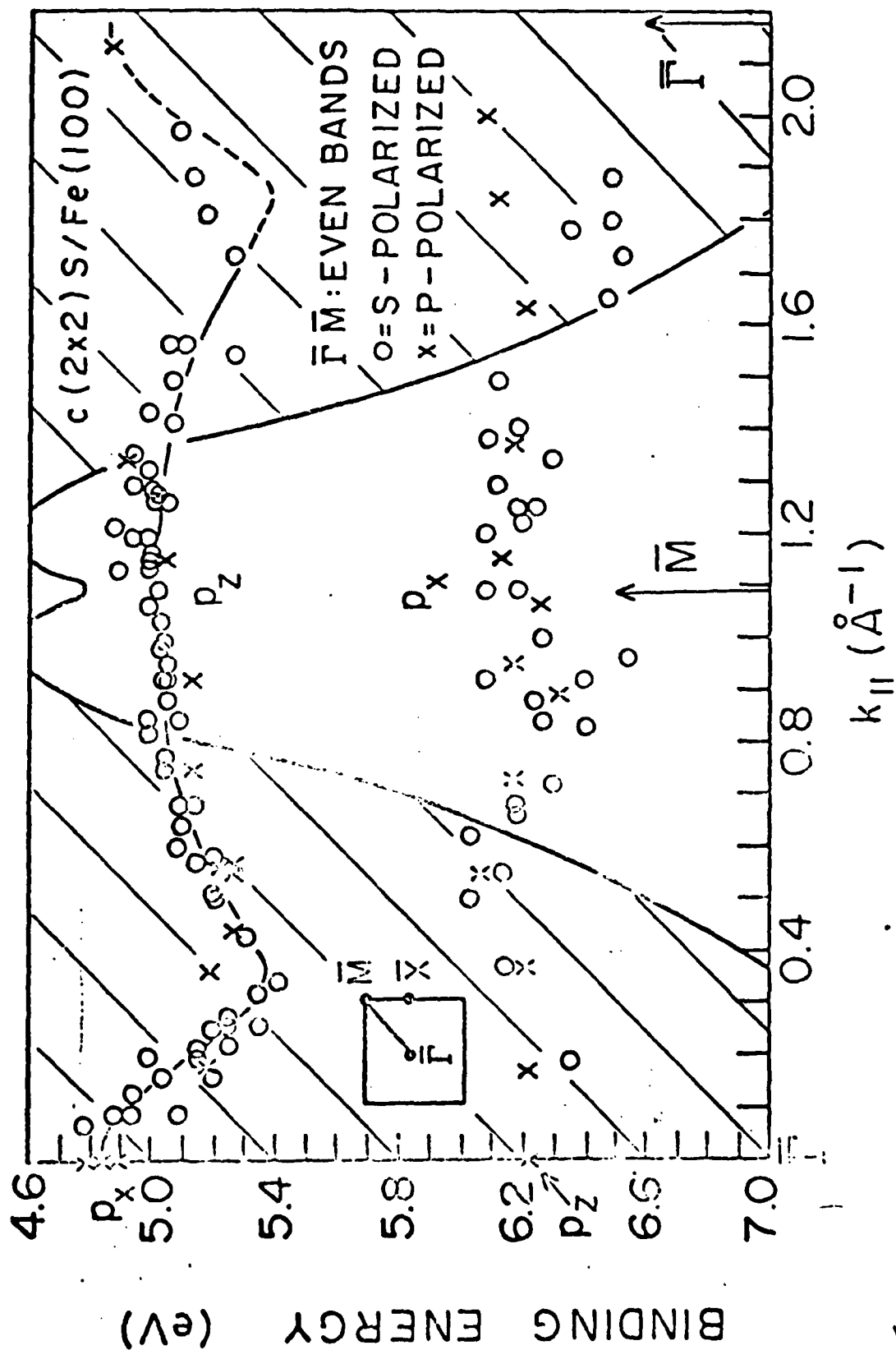


FIG. 3

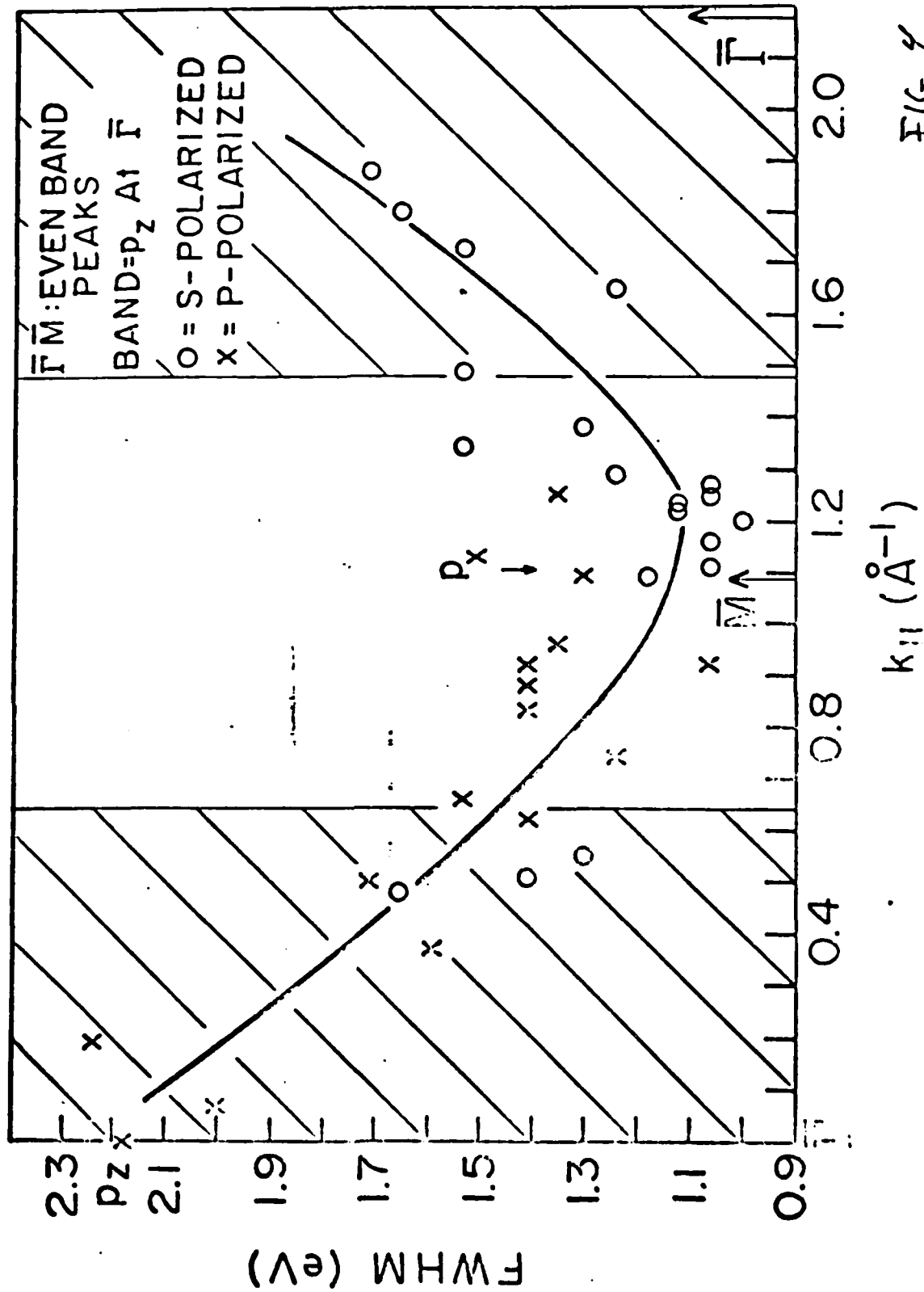


FIG. 4

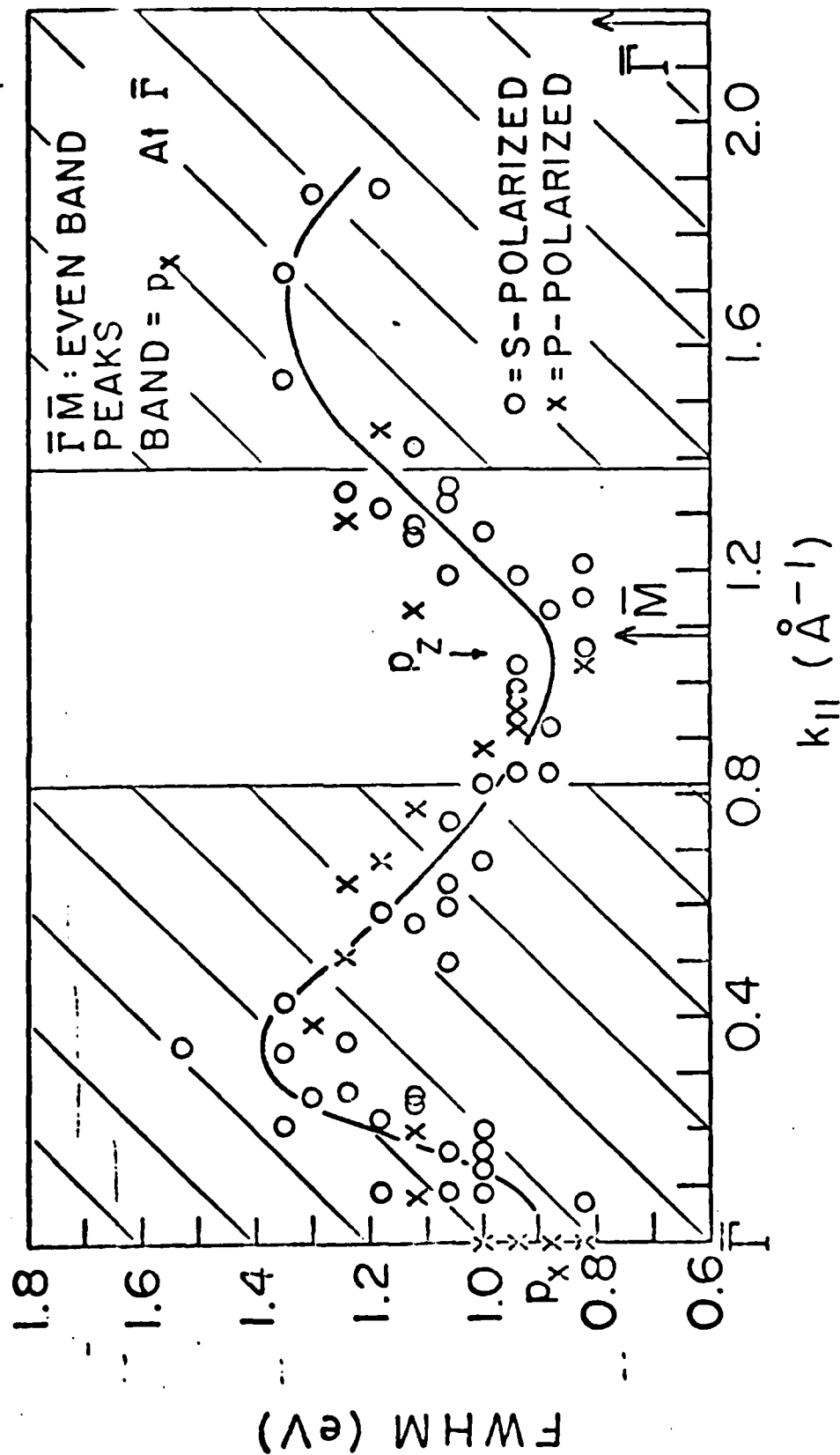


FIG. 5

